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Kinetics and Mechanism of Metal Nanoparticle Growth *via* Optical Extinction

Spectroscopy and Computational Modeling: The Curious Case of Colloidal Gold

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Abstract

An overarching computational framework unifying several optical theories to describe the temporal evolution of gold nanoparticles (GNPs) during a seeded growth process is presented. To achieve this, we used the inexpensive and widely available optical extinction spectroscopy, to obtain *quantitative* kinetic data. *In situ* spectra collected over a wide set of experimental conditions were regressed using the physical model, calculating light extinction by ensembles of GNPs during the growth process. This model provides temporal information on the size, shape, and concentration of the particles, and any electromagnetic interactions between them. Consequently, we were able to describe the mechanism of GNP growth and divide the process into distinct genesis periods. We provide explanations for several longstanding mysteries, *e.g.*, the phenomena responsible for the purple-greyish hue during the early stages of GNP growth, the complex interactions between nucleation, growth and aggregation events, and a clear distinction between agglomeration and electromagnetic interactions. The presented theoretical formalism has been developed in a generic fashion so that it can readily be adapted to other nanoparticulate formation scenarios such as the genesis of various metal nanoparticles.

Keywords

Gold nanoparticles, seeded growth, UV-Vis spectroscopy, computational modeling, kinetics and mechanism.

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3 Since Faraday's seminal work on the synthesis of colloidal gold nanoparticles (GNPs), there has been a
4 tremendous effort to explore various nanoparticle synthesis routes in order to obtain better control over
5 the properties of the final product.^{1,2} Every year numerous papers show up attempting to propose
6 mechanisms for particular synthesis pathways. Most of these studies try to interpret these complicated
7 processes in terms of simplified models and fail to describe the whole process, in particular when dealing
8 with a wide range of operating conditions. This invokes the need for more complete mechanistic
9 theoretical models. By performing global uncertainty/sensitivity analysis on such models one can map out
10 various outcomes of the process vs. different possible combinations of the operating conditions.³ Ideally,
11 this should be the first step in a predictive theory-driven synthesis of nanoparticulate systems.
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15 To develop a theoretical formalism with predictive capacity, extensive *in situ* experimental data over a
16 wide range of conditions has to be collected. In the case of nanoparticles, relatively expensive and
17 laborious characterization techniques such as *in situ* transmission electron microscopy (TEM),^{4,5} and
18 synchrotron-based X-ray scattering and X-ray absorption spectroscopy⁶⁻⁸ are typically employed. This is
19 probably because of the well-developed computational tools available for the analysis of the experimental
20 data (particularly in the case of X-ray based methods).⁹⁻¹² Despite this popularity, both the electron beam
21 and synchrotron light can drastically affect the system under investigation, *e.g.*, accelerate the process of
22 GNP formation and growth.^{4,5,8,13,14} For synchrotron-based methods, to circumvent this limitation one
23 solution is the application of liquid jets so that a fresh sample is probed throughout the process.^{8,15} This
24 method, however, adds to the complexity of the setup and does not allow for real-time measurements.¹⁵
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26 At the same time, optical extinction spectroscopy (OES) is rarely used to follow the formation of
27 nanoparticles in spite of being noninvasive,^{13,14} significantly less expensive, and widely available. Indeed,
28 to our knowledge, very few articles have tried to quantitatively employ this characterization method and
29 they are either dealing with relatively simple systems, where the particles behave as optically independent
30 entities, or they simply neglect the interparticle interactions (see below for further discussion).^{16,17} For this
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reason, there is a great need for a general and easily adaptable theoretical framework that utilizes the practical application of OES in the study of nanomaterial formation.

So far, several investigations have addressed the mechanistic aspects during the (seeded) growth of GNPs using various characterization techniques such as atomic force microscopy (AFM),^{5,14,18} electrophoretic measurements,^{19,20} redox potential/pH measurements,^{18–20} dynamic light scattering (DLS),^{14,19,21} *ex situ* TEM,^{4,5,7,14,19–23} *in situ* TEM,^{4,5} and X-ray scattering.^{6,7,13,23,24} Many of these studies follow the process also using *ex situ*^{5,19–22} or *in situ*^{14,23,24} UV-Vis spectroscopy but the information is treated merely qualitatively.

From the plethora of research, some of which was summarized above, we know that the processes of seeded growth is typically accompanied by nucleation of new particles.^{5,25} This could either be in a homogeneous fashion,²⁵ or in the close vicinity of the already present seed surface⁵ (so called true catalytic secondary nucleation²⁶ or, equivalently, near surface nucleation followed by particle mediated growth⁵). Additional complications arise from the possibility of agglomeration/aggregation invoked in many studies to describe the transient enhanced extinction in the wavelength range 600–800 nm, namely, the temporary purple-greyish colour of the suspension.^{7,18–20,27} Biggs *et al.*¹⁸ and Chow and Zukoski¹⁹ explained this in the light of the reduced colloidal stability in the presence of Au(III) in solution. Later, Rodriguez-Gonzalez and co-workers noticed that a homogeneous Au(III)→Au(I) reduction, followed by Au(I) diffusion toward the seed surface, and its subsequent disproportionation to Au(0) and Au(III) was more consistent with their experimental observations.²⁰ Along the same lines, several workers have presented strong evidence for the intermediacy of Au(I) in the reduction of Au(III) to metallic Au.^{6,21,28,29} Thus, it appears that Au(I) adsorption on the surface of GNPs tampers with their colloidal stability and as it is progressively reduced to Au(0), the surface is repopulated by the abundant citrate anions, and the colloidal stability recovers.^{19–21} Another notable observation comes from recent experimental and theoretical findings by Cheng *et al.* who found that the local supersaturation in the region at the seed-solution interface exceeded that in the bulk of the reaction medium.⁵ Furthermore, as soon as secondary

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3 nuclei form in the vicinity of the seed surface, the gold ions tend to accumulate in the interparticle gap,
4 replacing the citrate ions.⁵ This induces even further destabilization and brings the particles closer to each
5 other, giving rise to large numbers of GNPs interacting inside mesoscale superclusters, several times
6 larger than the individual particles.^{14,21,24}

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12 Beside the above phenomena, a third and somewhat less addressed complexity concerns the
13 electromagnetic interactions between the particles.^{14,23,24,30,31} As we discussed in the previous paragraph,
14 colloidal destabilization can bring particles closer to one another. This in turn provokes electromagnetic
15 coupling between the neighbouring particles.^{32,33} Plech *et al.*,¹³ and also Förster *et al.*²⁴ detected evidence
16 for such “correlated assemblies” using small-angle X-ray scattering (SAXS), while Mikhlin *et al.*¹⁴
17 physically detected such liquid-like mesostructures using AFM, DLS, and TEM. In the literature, this
18 effect has been frequently confused with agglomeration/aggregation wherein the particles are supposed to
19 be in contact with each other (throughout this work we stick to the IUPAC definitions for
20 agglomeration/coagulation and aggregation denoting the formation of physically and chemically bound
21 multi-particle associates, respectively³⁴). In our study, however, we explicitly distinguish between these
22 effects in the sense that closely spaced particles are considered to be in electromagnetic interaction (and
23 not agglomerated/aggregated) unless they touch each other (see Supporting Section 2).

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29 Here, we have developed an overarching computational framework, unifying various optical theories, to
30 describe the extinction of light by nanoparticles that may exhibit electromagnetic interactions. We applied
31 the approach to an *in situ* study on citrate-mediated seeded growth of GNPs while the theoretical
32 formalism can be employed in different scenarios such as for other metallic nanoparticles. With this
33 method, we rigorously identified the different mechanistic steps during the evolution of seeds toward final
34 particles, under several experimental conditions. The output was consistent with previous experimental
35 observations. We also provide cogent and comprehensive answers to a number of longstanding questions,
36 such as the phenomena responsible for the purple-greyish hue during the early stages of GNP growth, the
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complex interactions between nucleation and growth events, and a clear distinction between agglomeration and electromagnetic interactions.

Results and discussion

Computational framework

Dielectric function of nanosized gold and water (solvent)

The first step in developing an optical model for the extinction behavior of gold suspensions is the modification of the bulk dielectric function so that temperature and finite size effects are properly taken into account. For the bulk data, we used the dielectric function of gold recently measured by Yakubovsky *et al.* on a 25 nm thick film (measured wavelength range 300-2000 nm).³⁵ A smoothing spline was fitted to these data yielding the dielectric function of gold at room temperature every 1 nm (Figure 1). Intrinsic size effects for particles smaller than the mean free path of electrons in bulk gold were accounted for in the framework of the extended Drude model assuming size- and temperature-independent contribution from the interband transitions.^{32,36,37} Thus, the complex dielectric function of gold reads:

$$\epsilon(\omega, r, T) = \epsilon_{IB}(\omega) + \left[1 - \frac{\omega_p(T)^2}{\omega(\omega + i\Gamma(r, T))} \right] \quad (1)$$

where ϵ_{IB} represents the contribution of the interband transitions by the bound electrons while the term in the square brackets comes from the free-electron contributions. In the latter, ω_p is the temperature-dependent bulk plasma frequency (rad/s), $\omega = \frac{2\pi c}{\lambda}$ is the vacuum angular frequency of the incident light (rad/s; c and λ are the speed of light and wavelength in vacuum, respectively), and Γ is the temperature (T)- and size (equivalent spherical radius; r)-dependent damping frequency (rad/s) for the free electrons. The temperature dependence of ω_p can be estimated considering the thermal expansion of gold, which in turn reduces the density of the conduction (free) electrons:

$$\omega_P(T) = \frac{\omega_P(T_0)}{\sqrt{1 + \alpha_V(T - T_0)}} \quad (2)$$

Here, $T_0 = 298.15 \text{ K}$ is a reference temperature (room temperature), $\omega_P(T_0) = 1.37 \times 10^{16} \text{ rad/s}$,³⁵ and $\alpha_V = 4.17 \times 10^{-5} \text{ K}^{-1}$ is the volumetric thermal expansion coefficient of gold.³⁷

The damping of the free electrons arises from several processes including the interactions with phonons, electrons, lattice defects, grain boundaries, impurities, surface adsorbed species, and surfaces/interfaces themselves.^{32,36,38} The temperature dependences of the interactions with phonons (Γ_{e-ph}) and electrons (Γ_{e-e}) can be described as:³⁷

$$\Gamma_{e-ph}(T) = \Gamma_{e-ph}(T_0) \times \left[\frac{2}{5} + 4 \left(\frac{T}{\theta} \right)^5 \int_0^{\theta/T} \frac{z^4}{e^z - 1} dz \right] \quad (3)$$

$$\Gamma_{e-e}(\omega, T) = \frac{\pi^3 \Sigma \Delta}{12 \hbar E_F} \left[(k_B T)^2 + \left(\frac{\hbar \omega}{2\pi} \right)^2 \right] \quad (4)$$

In these equations $\Gamma_{e-ph}(T_0) = 7.09 \times 10^{13} \text{ rad/s}$ (back calculated from³⁵ $\Gamma_{bulk}(T_0) = 1.2686 \times 10^{14} \text{ rad/s}$), $\theta = 170 \text{ K}$ is the Debye temperature of gold, $\Sigma = 0.55$ is the Fermi-surface average of scattering, $\Delta = 0.77$ is the fractional Umklapp scattering, $E_F = 5.51 \text{ eV}$ is the Fermi energy, $\hbar$ is the reduced Planck constant, and k_B is the Boltzmann constant.³⁷ In addition to these two damping mechanisms, the size-dependent damping due to interactions with surfaces/interfaces, grain boundaries, and defects (the free path effect,^{32,36} FPE) can be estimated using the following phenomenological approach:

$$\Gamma_{FPE}(r) = A_{eff} \frac{v_f}{L_{eff}} \quad (5)$$

where $v_f = 1.4 \times 10^6 \text{ m/s}$ is the Fermi velocity of gold and $L_{eff} = \frac{4 \times \text{volume}}{\text{surface area}} \left(\frac{4}{3}r \text{ for spheres} \right)$ is the effective mean free path of electrons in nanoparticles with arbitrary shape.³⁹ Further, $A_{eff} \equiv \frac{4}{3}\eta$ where η accounts for the details of the scattering process and the additional contributions, *e.g.*, by defects,

adsorbed species, and grain boundaries,^{38,40,41} and the factor $\frac{4}{3}$ gives a typical proportionality constant 1 for surface-induced scattering as a function of radius in spherical nanoparticles (for which $\eta \equiv 1$).^{32,36} Here, the parameter η was calibrated using the volume-weighted mean particle radii of seeds and grown GNP estimated from the TEM micrographs (Supporting Section 3).⁴⁰ The regression of these two experimental spectra was done by fixing the mean radii and globally fitting η along with the aspect ratios of prolate-shaped particles ($\bar{\beta}$) for both seeds and grown GNPs using the Gans formalism in the range 400-800 nm. The value of η was constrained in the range [0.2,4].⁶⁻⁸ The fitted η values were used to derive a linear relation $\eta = \eta_0 + \eta_1 \bar{r}_{GNP}$ which was then used for all the intermediate spectra.

Having all the damping mechanisms in place one can calculate the overall damping frequency as^{32,36}

$$\Gamma = \Gamma_{e-ph} + \Gamma_{e-e} + \Gamma_{FPE} \quad (6)$$

In practice, we can estimate ϵ_{IB} by subtracting the bulk Drude expression at room temperature ($r \rightarrow \infty \Rightarrow \Gamma_{FPE} \rightarrow 0$) from the experimental dielectric function:

$$\epsilon_{IB}(\omega) = \epsilon_{experimental} - \left[1 - \frac{\omega_P(T_0)^2}{\omega(\omega + i\Gamma(\omega, r \rightarrow \infty, T_0))} \right] \quad (7)$$

Some workers have suggested that correcting only the imaginary part (of the dielectric function) for the intrinsic size effects provides superior fits to experimental data.⁴² However, our preliminary simulations proved the opposite in line with the work of Amendola and Meneghetti.⁴⁰ For this reason, throughout this work we will correct both the real and imaginary parts of ϵ .

The dielectric function of water at different temperatures was calculated according to the correlation by Fernández-Prini and Dooley.⁴³

Light extinction by ensembles of electromagnetically interacting GNPs

The extinction of light by an ensemble of noninteracting GNPs is typically described using the Mie theory (in case of spherical particles) or the Gans formalism in the quasi-static regime (spheroidal GNPs with

diameter $< \approx 30$ nm).^{40,42} In these theories, nanoparticles are assumed to experience only the external field due to the UV-Vis light source. However, more often than not, there are significant electromagnetic interactions between the particles.^{30,32,36} In other words, many nanoparticles experience a combination of the external field and the field induced by their neighboring particles (that is, all those inside the mesoscale supercluster embracing the particle). Particularly, in the case of metal nanoparticles synthesis (*e.g.*, growth of GNPs) experimental evidence support the presence of such interactions.^{14,24,30} In order to account for such interparticle interactions, there are two alternatives. One can take advantage of a plethora of *numerical* techniques employed to describe the optical extinction by (electromagnetically interacting) particle ensembles. This includes coupled dipole approximation,⁴⁴ generalized Mie theory,⁴⁵ and boundary element method⁴⁶ to name a few. An alternative approach is the application of effective medium theories (EMTs).^{36,47–49} While the former applies to any particle size and configuration, the latter is applicable only in the quasi-static regime. Nevertheless, the numerical approaches are computationally prohibitive, particularly for ensembles with large numbers of particles. Therefore, considering the small size of the GNPs in the current study, we chose to employ an EMT formalism to account for the possible electromagnetic interactions between the particles. This allows us to handle the large number of spectra collected during the seeded growth process.

In view of the discussion in the earlier paragraph, the optical response of ensembles composed by interacting GNPs is described using the Maxwell-Garnett effective medium theory, with retarded polarization effects incorporated following Granqvist and Hunderi.^{47,48} The interacting GNPs are presumed to form spherical domains wherein their local number concentration exceeds that of the bulk solution (*i.e.*, that averaged over the entire suspension; Figure 2a inset). The presence of such dense liquid-like superclusters (SCs) has been shown by a variety of characterization techniques (*e.g.*, DLS, AFM, and *in situ* TEM).^{4,14} Schatz and colleagues have used this picture to describe the extinction by arrays of plasmonic nanoparticles, *i.e.*, DNA-linked GNP clusters with volume fractions between 1–20%.^{44,49}

Granqvist and Hunderi extended the Maxwell-Garnett EMT by introducing a phase factor in the Lorentz local-field equation.^{47,48} Doing that, they arrived at the following equation for the effective dielectric function ($\bar{\epsilon}$) of an ensemble of nanoparticles embedded in a surrounding medium with dielectric permittivity ϵ_m :

$$\bar{\epsilon} = \epsilon_m \frac{1 + (1 - \frac{1}{3}e^{i\delta})\sum_j f_j \alpha'_j}{1 - \frac{1}{3}e^{i\delta}\sum_j f_j \alpha'_j} \quad (8)$$

with

$$\alpha'_j \equiv \frac{4\pi\alpha_j}{V_j} = \frac{1}{3} \sum_{i=1}^3 \frac{\epsilon_j - \epsilon_m}{\epsilon_m + L_{ij}(\epsilon_j - \epsilon_m)} \quad (9)$$

In these equations f_j denotes the fractional filling factors (volume fractions) of various particle classes with $\sum_j f_j = f$, where f is the total volume fraction of particles within the effective medium (individual superclusters). Additionally, α_j denotes the polarizability of particle j with a volume (V_j), and L_{ij} represents the triplet of depolarization factors along the different axes of the prolate spheroid j .^{47,48} Using these quantities, for randomly oriented spheroids we can estimate the average volume-normalized polarizability (α'_j).^{32,47,48} In Eq. (8), $e^{i\delta}$ is a phase factor that accounts for the retarded nature of interaction with the depolarizing field and can be estimated knowing the mean centre-to-centre distance between the particles:

$$\delta = \frac{2\pi\sqrt{\bar{\epsilon}}\bar{d}_{cc}}{\lambda} \quad (10)$$

Assuming a uniform distribution of particles throughout the effective medium²⁴ (Figure 2a inset), the center-to-center distance between the particles can be estimated as:^{24,50}

$$\bar{d}_{cc} = 2\bar{r}_{GNP} \times \sqrt[3]{\frac{\pi}{\sqrt{18}f}} \quad (11)$$

In this equation, $\bar{r}_{GNP}$ is the average equivalent spherical radius of the GNPs and the factor $\frac{\pi}{\sqrt{18}}$ is the close packing density of the equal spherical domains embracing the individual GNPs (dotted black circles surrounding individual GNPs in Figure 2a inset). Considering the dependence of δ on $\bar{\epsilon}$, an iterative procedure is necessary to calculate the $\bar{\epsilon}$, starting with the non-retarded $\bar{\epsilon}$ as an initial guess.^{47,48}

A representative effective dielectric permittivity at 70°C for a supercluster of 10 nm GNPs in water with $f = 0.2$ is shown in Figure 2, calculated using both Maxwell-Garnet theory and its retarded extension by Granqvist and Hunderi.^{47,48} Once we have the effective dielectric function of the spherical SCs, we can calculate the extinction cross section of noninteracting SCs using the Mie theory. Schatz *et al.* applied this method to calculate the extinction by DNA-linked nanoparticles and showed that the results match very well with those from the more rigorous coupled dipole approximation.⁴⁹

Overall modeling workflow and regression to experimental spectra

Generally, the optical extinction by colloidal metal nanoparticles may arise from two sources. The first is the extinction by well-separated nanoparticles whose interaction with the incoming light is practically independent from one another.^{32,40} The second contribution comes from nanoparticles lying close to each other (inside liquid-like superclusters, SCs, but not touching), experiencing a superposition of the external field with the mean field produced by all the neighbouring particles. Accounting for both possibilities in a suspension undergoing kinetic evolution requires the application of the Gans formalism^{32,40} for the former and a retarded effective medium theory (EMT)/Mie scattering framework^{47–49} for the latter. Hereafter, we refer to this combined Gans + EMT/Mie framework as the GEM model. Using this model, five physically well-defined parameters have to be estimated from regression to experimental spectra: $\bar{r}_{GNP}$ (average equivalent spherical radius), $\bar{\beta}$ (mean major-to-minor axis ratio), x_{SC} (number fraction of SCs out of all

the scatterers, *i.e.*, SCs + noninteracting GNPs), f (filling factor, *i.e.*, the volume fraction of GNPs inside SCs), and $\bar{r}_{SC}$ (average radius of spherical SCs).

Neglecting the electromagnetic interactions between the particles one can use the Gans formalism for prolate spheroids with only $\bar{r}_{GNP}$ and $\bar{\beta}$ as the parameters to be determined by regression.^{32,40} Using either model (Gans or GEM), a globalized bounded Nelder-Mead optimization scheme was employed for the regression to the experimental data.⁵¹ The 95% confidence intervals on various regression parameters and on different model outputs were obtained by a heuristic approach described by Schwaab *et al.*⁵² As the optical interaction effects disappear the EMT-specific parameters (x_{SC} , f , and r_{SC}) lose their meaning and the common parameters ($\bar{r}_{GNP}$ and $\bar{\beta}$) approach to the same values for regressions with both the GEM and the Gans model. In this case, we selected the Gans formalism as the superior model since it has fewer parameters and provides exactly similar optimization results as the GEM formalism.

All the computational codes, both for the calculation of optical extinction and the regression of the experimental spectra, were developed in MATLAB R2017b (available in the Supporting Information). Mie scattering calculations were implemented using the MATLAB/Octave code written by Demers *et al.*⁵³ Figure 3 schematically summarizes the overall workflow, including the theory and the regression steps, in a flow chart. See Supporting Section 2 for further details on the theoretical framework and the regression protocol.

Results from OES analysis *via* physical modeling

With the summary in the previous section, we are ready to examine the outcome of the *in situ* measurements conducted in the current study. In the rest of this paper, we will primarily focus on the results for the seeds synthesized with 15% citric acid and grown at 70°C (experiment 15:85-70°C; see Section on Computational framework and Supporting Section 1). Results for other experiments, analysed using our overarching model, are either mechanistically similar or simpler and are discussed in Supporting Sections 4-5.

Figure 4a shows representative regressions for the experiment 15:85-70°C (see Supporting Figs. 4-8 for all the temporal regressions). We see that applying the Gans theory (*i.e.*, neglecting the optical interaction effects) only provides good regressions at early and later times (Figure 4a spectra at 0, 20, 80, 750, 1130, 1500 s and Figure 4b). During these periods, the GEM model describes the data equally well and yields the same optimal values, as those obtained from the Gans theory, for the common parameters $\bar{r}_{GNP}$, $\bar{\beta}$ (Supporting Figure 30). Nevertheless, the regression becomes insensitive to the EMT-specific parameters (x_{SC} , f , and r_{SC} ; Supporting Section 8) and thus, the Gans formalism should be selected to avoid overfitting. During the intermediate period (spectra at 150 to 670 s), however, it is crucial to account for the electromagnetic interactions and the GEM framework has to be chosen (Figure 4b; see the Section on Computational framework and Supporting Section 2 for further details on model selection). With these considerations in mind, our theoretical framework provides excellent regressions to the experimental spectra throughout the kinetic process. Quantitatively, the range-normalized root mean square errors (NRMSE) are invariably less than 2% for all the regressions while the deviations from experimental data at individual wavelengths and time points are never more than 5% of the extinction range (Figure 4b and c, respectively).

Figure 5 presents the temporal evolution of the optimized model parameters (a-e) and the particle number concentration (f) for the experiment 15:85-70°C. In this figure, the red open circles represent the outputs of the GEM model regression whereas the black dots are those corresponding to the selected model along with their heuristically estimated⁵² 95% confidence bounds (see the Section on Computation framework and Supporting Section 8 for details). Figure 6 also provides some additional kinetic outputs obtained from regressing the experimental spectra (a-c), representative recorded spectra (d), the evolution of peak width at half-maximum (PWHM) calculated from the experimental spectra according to Natan *et al.*⁵⁴ (e; twice the difference between λ_{LSPR} and the wavelength to its red with an extinction half the value at LSPR), and the *in situ* measured solution pH and reduction potential (f; Eh vs. Ag/AgCl/c(KCl) = 3

mol/L). The grey-to-white shaded regions in Figs. 3b, 4, and 5 (denoted by Roman) characterize the various mechanistic steps as discussed below.

Figure 5a,b,f show that the GEM model approaches the Gans formalism when the interaction effects are negligible (that is, when % GNP in SCs approaches zero; 5b). We can see this self-consistent behaviour more clearly in Supporting Figure 30 where the common parameters/outputs of the two models ($\bar{r}_{GNP}$, $\bar{\beta}$, GNP number concentration, and effective density) are plotted on the same axes. As expected, the discrepancy grows when the interaction effects become more prominent and it reaches a maximum around the same time the percentage of GNPs inside SCs is the highest. With the self-consistency checked, we can now scrutinize the temporal evolution during the seeded growth of GNPs by dividing the overall process time into five regions, as discussed below.

In region (I) (0-150 s), as soon as the concentrated Au(III) solution is injected into the seed suspension (Figure 6d; the spectrum at 20 s) $\bar{r}_{GNP}$ drops from 7.4 to 6.1 nm (Figure 5a) while the number concentration of particles almost doubles (Figure 5f). This implies the occurrence of a nucleation event which quickly decelerates as a result of pH change (1.7 in the 20 mM Au(III) solution to 5.5 in the reaction medium at 70°C) converting the highly reactive $[\text{AuCl}_4]^-$ species into its less reactive, hydrolysed counterparts ($[\text{AuCl}_{4-x}(\text{OH})_x]^-$; $x = 1-4$).^{7,55} The sudden leap in PWHM and its subsequent stabilization correlates with this observation (Figure 6e). Presumably, the new particles are generated by primary and secondary nucleation (*i.e.*, nucleation independent from or induced by the presence of already formed gold nanoparticles, respectively²⁶), as both mechanisms are possible under this operating condition. More specifically, the temperature, pH and number concentration of the seeds lie within a range where both nucleation types are viable (note that at the point of injection the high local supersaturation could induce an even faster nucleation).^{5,25} Alternatively, by lowering the temperature to 20°C (in a suspension prepared by only Na_3Cit) one can minimize primary nucleation (*i.e.*, preserve the particle number concentration).⁵ In the latter case, all the injected Au(III) would be spent to enlarge the seeds through catalytic secondary nucleation and molecular growth (note that compared to primary nucleation, both

processes have smaller free energy barriers²⁶).⁵ Indeed, Wuithschick *et al.* employed this notion to determine the reaction time at which primary nucleation stops during the method of Turkevich.⁷

Another notable feature in region (I) is the formation of more anisotropic nanoparticles (increase in $\bar{\beta}$ from 1.25 to 1.5; Figure 5b) which is also documented in TEM observations by other workers.^{5,22,25,56} Such anisotropic secondary particles can arise due to either slow agglomeration/aggregation,⁵⁶ or secondary nucleation.⁵ In this case, considering the short duration of region (I) and the near-bulk effective density of the population (Figure 6a), a secondary nucleation followed by integration to the seeds, *via* interparticle molecular growth, seems to be responsible for the anisotropy (see Supporting Section 2 for the protocol to estimate effective density).⁵ A detailed discussion regarding the origins of anisotropy in secondary particles is presented in the classic paper by Enustun and Turkevich.⁵⁶

After the nucleation event at the beginning of region (I), ensuing the reduced colloidal stability (due to Au(I) adsorption on the surface) and increased number concentration, there is a quiescent period during which particles start to gradually approach each other. This gives rise to electromagnetic interaction effects and the appearance of mesoscale liquid-like superclusters (Figure 5c-e and Figure 6b,c; Figure 6d,e enhanced extinction in the wavelength range 600-800 nm and peak broadening).¹⁴ Looking at the potential measurements (Figure 6f), we see that the pH continuously drops which is due to the injection of chloroauric acid solution and $[AuCl_4]^- \rightarrow Au(I)$ reduction by citrate.^{21,55} The latter, which dominates after the mixing period (probably less than a second), provides growth units/monomers for the densification of secondary particles (*via* molecular growth and neck formation⁵) in addition to a subsequent nucleation event which happens in region (II) (see below). Looking at the Eh data (Figure 6f) in region (I), and knowing that the Au(I)/Au(0) couple mainly determines the potential of the gold electrode,^{20,28} we understand that the quick initial drop in potential is related to the consumption of Au(I) by nucleation and molecular growth. Following this shallow drop, Eh rises back up which indicates the build-up of Au(I) consistent with the pH behaviour discussed earlier.

In region (II) (150-350 s) the formation of Au(0) accelerates (Figure 6a) due to a burst of new particles increasing the number concentration (Figure 5f) and lowering $\bar{r}_{GNP}$ (Figure 5a). This corresponds to a second nucleation event (both primary and secondary nucleation). One major difference compared to region (I) is the rapidly dropping effective density of GNPs (Figure 6a) which indicates that most of the Au(III) precursor is consumed in nucleation rather than molecular growth. This way, inside the resultant anisotropic secondary particles, mainly physical bonds hold primary particles together. We may identify these secondary particles as agglomerates but we should note that the mechanism behind their formation is true catalytic secondary nucleation^{5,26} and not agglomeration.

As we mentioned earlier, in region (I) the concentration of Au(I) builds up,^{21,29} which in turn provides a high supersaturation level that allows for significant primary nucleation alongside secondary nucleation in region (II). Concurrent with the rapid increase in number concentration and in the presence of surface-adsorbed Au(I), colloidal stability decreases further and more GNPs approach each other to form liquid-like superclusters (Figure 5c-e and Figure 6b,c; Figure 6d enhanced extinction in 600-800 nm).

Nanoparticles assemble into mesoscale structures ~ 350 nm in diameter (Figure 5e) with an average centre-to-centre distance ~ 15 nm ($\cong 3 \bar{r}_{GNP}$) between the GNPs (Figure 6c). The presence of both significant electromagnetic interactions and elongated nanoparticle agglomerates induces a two-fold rise in the experimentally measured PWHM (Figure 6e).

Consulting Figure 6f in region (II), the pH remains almost constant although the reduction of Au(III) by citrate releases protons.^{21,55} To explain this, we note that most of the highly reactive $[\text{AuCl}_4]^-$ species has already converted either into Au(I) or $[\text{AuCl}_{4-x}(\text{OH})_x]^-$. For this reason, Au(III) speciation is shifted toward $[\text{AuCl}_4]^-$ (Le Chatelier's principle), releasing OH^- :

This shift counterbalances the pH decreasing effect of Au(III) reduction and remains until the end of the process, as witnessed by the continuous slow increase in pH. Finally, with Au(I)/Au(0) as the chief

potential determining couple,^{20,28} the gradual decrease in E_h (Figure 6f) implies a continuous $Au(I) \rightarrow Au(0)$ reaction in region (II).

Region (III) (350-590 s) is accompanied by a precipitous drop in the number concentration of GNPs (Figure 5f) which come together and produce larger, secondary particles around 9 nm in radius (Figure 5a). These secondary particles are predicted to have a quite spherical shape (Figure 5b) and are of lower effective density compared to bulk gold (Figure 6a). Therefore, they appear to be randomly packed fluffy agglomerates, whose morphology results from fast agglomeration under reduced colloidal stability.^{19,20,56} The high number concentration at the beginning of this period supports such a fast coagulation process.^{7,18–20,56} Concurrently, growth continues to consume ionic Au as evidenced by the continuous increase in $Au(0)$ concentration (Figure 6a).

Looking at the state of particle-particle interaction, it continues to grow (Figure 6b) and reaches a maximum at the end of this period (more than 70% of GNPs experiencing electromagnetic interactions with neighbouring particles). This is consistent with the continued enhancement of extinction in the wavelength range 600-800 (the transient purple-greyish hue observed in the evolving suspension; Figure 6d). Consulting Figure 6e, initially PWHM does not significantly change, but toward the end of this period, it rises toward a maximum of more than 300 nm (more than threefold the value in the seed spectrum). To explain this, we note that at the beginning the formation of more spherical agglomerates counteracts the peak broadening caused by enhanced electromagnetic interactions. Yet, eventually interaction effects dominate and broaden the localized surface plasmon resonance (LSPR) band (Figure 6e).

In region (III), the majority of $Au(III)$ is in the hydrolysed form (considering the pH level, Figure 6f) and they gradually reduce to $Au(I)$, either directly or *via* $[AuCl_4]^-$.⁵⁵ Hence, unlike region (I) the level of supersaturation ($Au(I)$ activity) is comparatively low. Consequently, contrary to the dense secondary particles in region (I), the agglomerates forming in region (III) do not have as extensive chemical bonds

and they are less dense (Figure 6a). Towards the end of this region, Eh decreases quickly indicating the onset of another nucleation event, manifesting in region (IV) (Figure 6f).

In region (IV) (590-750 s) the number concentration rises once again (Figure 5f) and $\bar{r}_{GNP}$ drops (Figure 5a). Meanwhile, $\bar{\beta}$ rapidly increases due to the reappearance of anisotropic secondary particles. We can describe these observations by another nucleation event. Here, considering the relatively low supersaturation degrees (Figure 6f), the energetically more favourable secondary nucleation is probably more significant than primary nucleation. A second mechanism that can account for the increased number concentration is the (partial) peptization (*i.e.*, redispersion of agglomerated particles back to colloidal stable primary particles³⁴) of the agglomerates formed in region (III). Chemical bond formation between primary particles inside these agglomerates gives rise to denser secondary particles (Figure 6a). During this compaction, the loosely bound primary particles would have a chance to repeptize. This is assisted by the recovered colloidal stability due to the relatively low particle number concentration at the end of region (III) (Figure 5f) and the lower level of Au(I) (Figure 6f). Complementary evidence for the regained colloidal stability comes from the rapidly disappearing interaction effects (Figure 5c,d and Figure 6b,c). As the interaction effects vanish, PWHM decreases as well, with a deceleration towards the end of the period (Figure 6d), the latter being due to the reappearance of anisotropic entities (Figure 5b).

In the last temporal region (750-1500 s), there is an abrupt drop in the number concentration (Figure 5f), and a fast rise in $\bar{r}_{GNP}$ (Figure 5a) and the average effective density (Figure 6a). Notably, Au(0) concentration does not perceptibly increase anymore (Figure 6a) implying an almost complete depletion of supersaturation. Eh being very close to its final equilibrium value further corroborates this hypothesis (Figure 6f). Hence, this period is dominated by an Ostwald ripening event (the amorphous nature of newly formed GNPs, as documented by Loh *et al.*,⁴ can help the dissolution of small nanoparticles). Thus, larger particles grow at the expense of smaller particles and agglomerates coalesce to structures that are denser (Figure 6a). In this period, coalescence along with intra-particle ripening render the particles more

spherical.^{5,22} Finally, in the absence of electromagnetic interactions, the two optical theories (GEM and Gans) predict similar outputs (Supporting Figure 30).

Figure 7 schematically summarizes the mechanistic picture presented earlier, enumerating the most prominent events in each temporal region. In this scheme, the degree of overlap between primary particles inside secondary particles is proportionate to the effective density of the latter (*i.e.*, the more the overlap, the higher the effective density). Note that molecular growth, defined as particle enlargement by the addition of molecularly sized entities, can happen as long as the system is supersaturated.²⁶ In region (V), this could be in the form of Ostwald/interparticle ripening.

Corroborating evidence from principal component analysis

Principal component analysis (PCA) is a useful and accessible tool to identify the major contributors to an overall signal.^{57,58} For an evolving colloidal suspension, the optical response can be decomposed into linearly uncorrelated variables, called principal components (PCs), giving coefficients (or loadings) with their corresponding temporal scores. In simple words, each coefficient represents the spectral signature of a PC while the score correlates with the weight (significance) of that PC at a specific time. PCA has a limitation in the sense that each spectrum is assumed to be a linear combination of several pure spectra. A tacit assumption in the previous statement is the constancy of the pure spectra (over time), which does not hold for a growing colloidal metal suspension. Therefore, PCA would detect artificial compounds, the linear combinations of which give the temporal spectra. Nevertheless, it is not possible to assign the coefficients to particular species.⁵⁷ In spite of these limitations, PCA allows for a model-free estimation of the number of contributing phenomena and provides rough optical signatures for each of them.

With the introduction above in mind, PCA over a spectral range 400-800 nm using the centered extinction data from the experiment 15:85-70°C (Figure 8) indicates that there are three main contributors while the fourth PC is practically capturing noise (as implied by its noisy coefficient and low score throughout the process). Note that there is no contribution from the dissolved ionic gold species nor from the organic

compounds in the selected spectral range.^{7,28} Therefore, only three PCs, all originating from the colloidal nanoparticles, capture > 99.8% of the temporal variation in the spectra with individual contributions 75.9, 22.8, 1.3% for PCs 1 to 3, respectively.

Taking a closer look at the coefficient plot (Figure 8a) reveals that the first PC (red full circles) is mainly related to individual GNPs with their LSPR band around 520 nm. The corresponding score plot (Figure 8b) indicates a monotonic evolution toward the final GNPs which bear more Au(0). This is consistent with the continuously increasing concentration of atomic gold shown in Figure 6a.

The second PC (Figure 8a; gray full circles) exhibits an inverse behavior close to the LSPR band (plasmon damping) while it correlates with the enhanced extinction in the range 600-800 nm. The corresponding score grows to a maximum and drops subsequently (Figure 8b). Thus, this PC majorly represents the electromagnetic interactions between the particles that appear early on, grow as the particles approach each other, and fade out as they peptize back to noninteracting scatterers. Mikhlin *et al.*¹⁴ identified a very similar temporal evolution during the one-pot synthesis of GNPs, where large (100-500 nm) three-dimensional networks of GNPs suspended in aqueous droplets appeared early on and disintegrated as the process proceeded to the end.

Finally, the third PC (Figure 8a; purple full circles) demonstrates a similar coefficient behavior as PC2 but with a narrower peak around 580 nm and a sharper contrast between this peak and the LSPR-damping band. The contrast signifies the distinction between longitudinal and transversal extinction cross sections in prolate-shaped particles. Therefore, this PC can mainly be ascribed to the particle shape evolution that dampens the LSPR band and enhances the extinction in the red region. Looking at Figure 8b, the temporal variation in the corresponding score plot correlates quite closely with the evolution observed in $\bar{\beta}$ (Figure 5b).

To summarize, the collective nonlinear combination of the three effects identified by PCA (*i.e.*, the extinction by individual GNPs as related to their Au(0) content, the particle aspect ratio, and the

electromagnetic interactions between the GNPs) dictates the temporal optical behavior of the particle ensemble. This nonlinear (and correlated) dependence does not allow for a one-to-one quantitative assignment between the PCs and the physical characteristics. That is why we tackled the problem directly adopting the nonlinear regression of a physicochemical model to the experimental data. Nevertheless, as we demonstrated earlier PCA does provide qualitative insight about the physics of the problem and provides support for the proposed theoretical framework. Results from PCA on other datasets exhibit similar resemblance to the output of the optical modeling framework and they are presented in Supporting Section 7.

Conclusions

In summary, we developed a comprehensive theoretical framework to extract kinetic and mechanistic information about the seeded growth of gold nanoparticles from time-resolved *in situ* optical extinction spectroscopy (OES). When compared to more sophisticated and expensive characterization techniques such as SAXS and *in situ* TEM, OES is appealing due to its availability, low cost, and relatively straightforward data collection procedure under various operating conditions. So far, the quantitative application of this technique was hampered by the lack of a complete theoretical formalism capable of extracting key temporal kinetic information like particle size, shape, and concentration, as well as the state of particle-particle interaction (mesoscale aspects). In this article, we drew on the extensive previous research in the field and developed a physical model to describe the optical response of a growing gold sol. We demystified the complexity of the process, which involves several temporally overlapping subprocesses, *e.g.* primary and secondary nucleation, molecular growth, agglomeration, and Ostwald ripening. We observed similar events for a wide range of experiments (*i.e.*, six sets of data at different T and pH) and presented mechanistic pathways to account for the various trends observed in the outputs of the spectral regression. In this respect, we identified the role of nucleation events accompanying the particle enlargement process. Moreover, we showed that the particle enlargement occurs *via* a combination of molecular growth (in the form of Ostwald ripening, particularly close to the end of the

process), secondary nucleation, and agglomeration. We further identified instances of peptization consistent with the previous experimental evidence reported by other workers.^{18–20} We also addressed the longstanding question about the nature of moieties responsible for the purple-greyish color during the growth of gold nanoparticles. This was determined by distinguishing between the optical signatures of electromagnetic interactions between the particles inside liquid-like superclusters, from that of relatively small fluffy agglomerates. Finally, our theoretical formalism was developed in a generic form so that it can also be applied to other nanoparticulate systems such as various metal nanoparticles.

Experimental

Materials

Metallic gold foil (99.99% pure) was purchased from Nuova Franco Suisse Italia. Hydrogen chloride (37 wt. % in H₂O, 99.999% trace metals basis), nitric acid (70% HNO₃, ≥99.999% trace metals basis), sodium citrate tribasic dihydrate (Na₃Cit.2H₂O, ACS reagent ≥99.0%), and citric acid (H₃Cit, ACS reagent ≥99.5%) were purchased from Sigma Aldrich. Ultrapure water (18.2 MΩ.cm, MilliQ) was used throughout the experiments. All the glassware and PTFE-coated magnetic stirring bars were cleaned with freshly prepared *aqua regia* and rinsed thoroughly with MilliQ water before each experiment. A stock solution of HAuCl₄ in water was prepared according to the procedure by Gross⁵⁹ and used in all the syntheses. Fresh solutions of HAuCl₄ and citrate buffer (with the desired concentrations) were prepared before each experiment and stored in tightly closed glass bottles.

Synthesis of GNP seeds and subsequent growth experiments

Gold nanoparticle seeds were prepared by injecting 1 mL of a 50 mM HAuCl₄ aqueous solution into 499 mL boiling solution of 2 mM citrate buffer under intensive stirring. The buffer's pH was tuned by adjusting the molar ratio citric acid/trisodium citrate (0%:100%, 15%:85%, and 25%:75%). We then used these particles in a seeded growth process, the kinetics of which was of interest. For this purpose, 0.75 mL 20 mM HAuCl₄ solution was rapidly injected into 60 mL of a seed suspension (under vigorous stirring) at

different temperatures (40, 60, 65, 70°C). The temporal evolution of the system was followed by UV-Vis spectroscopy (one spectrum every 20 s for the experiments 25:75-40°C and 0:100-70°C, and every 10 s for the rest of the experiments), reduction potential (Eh) measurement, and pH measurement (Eh and pH data points collected every two seconds). Six sets of experimental data were collected under various conditions (T and pH) using different seed suspensions. This includes experiments at 60, 65, and 70°C using the 15%:85%-buffer seed, experiments at 70°C using the 25%:75%- and 0%:100%-buffer seeds, and an experiment at 40°C using the 25%:75%-buffer seed suspension. Reference to each experiment denotes the buffer ratio followed by the experimental temperature, *e.g.*, 15:85-70°C (experiment using 15%:85%-buffer seed at 70°C). See Supporting Section 1 for further details on the kinetic experiments.

Characterization

The volume-averaged equivalent spherical radius for the seeds and grown GNP were found by TEM (JEOL-2010), measuring the semi-major and semi-minor axes of at least 100 particles using Fiji package and assuming prolate shaped particles (the axis perpendicular to the image is taken as a minor axis).^{54,60,61}

The TEM samples were prepared following the protocol recommended by Parak *et al.*⁶¹ *In situ* UV-Vis spectra were collected using an Ocean Optics PEEK immersion probe with 1 cm optical path length (pure water was used as the reference). The probe was connected to a DT-mini-2-GS UV-Vis-NIR light source and a USB2000+XR1 spectrometer, both from Ocean Optics. Each spectrum was an average of four 2.5-second (5 s for the data in 0:100-70°C and 25:75-40°C experiments) acquisitions smoothed with a boxcar width two. Measurements of pH and Eh (vs. Ag/AgCl/c(KCl) = 3 mol/L) were done using a pH glass electrode (Unitrode Pt 1000) and a combined gold ring electrode, respectively, provided by Metrohm AG.

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Associated content

Preprint version available: Andalibi, M.R.; Wokaun, A.; Bowen, P.; Testino, A. Kinetics and Mechanism of Gold Nanoparticle Growth Studied *via* Optical Extinction Spectroscopy and Computational Modelling. 2019, *arXiv*: 1903.06206. <https://arxiv.org/abs/1903.06206> (accessed Sept 04, 2019).

Supporting Information Available: Additional details on experimental and computational procedures, TEM micrographs of all the samples along with their particle size distributions, outputs and discussion for datasets not explored in the main text, convergence of the two optical models to the same output, discussion on confidence bounds obtained during regression on experimental data, and fully-commented MATLAB codes for the entire computational workflow. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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Figure captions

Figure 1. Contributions of the interband transitions (bound electrons) and the free electrons to the real (a) and imaginary (b) parts of the gold’s bulk dielectric function taken from Yakubovsky *et al.*³⁵ For comparison with the bulk data, the size- and temperature- corrected ϵ_{GNP} are also shown for prolate-shaped GNPs with 5 nm radius and aspect ratio 1.2 at $T = 70^{\circ}\text{C}$ using $A_{eff} = 4/3$.

Figure 2. Real (a) and imaginary (b) parts of the dielectric function for an effective medium composed of 20% (by volume) GNPs with $\bar{r}_{GNP} = 5\text{ nm}$ and aspect ratio 1.2 dispersed in water calculated using the Maxwell-Garnett (MG) and retarded effective medium theories at 70°C ($A_{eff} = 4/3$), normalized by the dielectric function of water. The inset in (a) is the schematic representation of an ensemble of electromagnetically interacting gold nanoparticles (yellow dots) composing a dense liquid-like supercluster (SC; large dashed circle in dark gray). Each black dotted circle around individual GNPs represents the portion of SC volume per particle.

Figure 3. Flowchart summarizing the overall computational framework, including the theory and the regression steps (with the names of the corresponding MATLAB scripts, *.m, wherever applicable). Here, C_t is the total number concentration of the scatterers (noninteracting GNPs + SCs), l is the optical path length, Ext is the overall optical extinction of the sol, and σ_{Gans} and $\sigma_{EMT/Mie}$ are the extinction cross sections of the noninteracting GNPs and SCs, respectively.

Figure 4. Summary of spectral regressions and their quality (experiment 15:85-70°C). (a) Representative experimental UV-Vis spectra (cyan curves composed of several open circles) and their corresponding theoretical fits using the Gans theory (red dashed lines) and the selected model (black lines). (b) Range-normalized root mean square error (NRMSE) for the temporal regressions using the two models. The grey-to-white shaded regions characterize various mechanistic steps (denoted by Roman numerals) as discussed in the main text. (c) Range-normalized deviations from experimental data for individual wavelengths and temporal points (obtained from regressions by the selected model).

Figure 5. Kinetics of gold nanoparticle growth (experiment 15:85-70°C) from *in situ* UV-Vis spectroscopy and model regression. (a-e) Regressed physical parameters (and their corresponding 95% confidence bounds found by a heuristic search method⁵²) including mean particle radius (a), mean particle aspect ratio (b), number fraction of liquid-like superclusters (c), volume fraction of particles in superclusters (d), and mean supercluster radius (e). (f) Temporal particle number concentration (along with 95% confidence bounds⁵²) obtained from scaling the calculated extinction cross sections with the experimental spectra. Legends are common in all the plots and the grey-to-white shaded regions characterize various mechanistic steps (denoted by Roman numerals in the first plot) as discussed in the main text.

Figure 6. Complementary kinetic data (experiment 15:85-70°C) from *in situ* UV-Vis spectroscopy and electrochemical potential measurements. (a) Gold nanoparticle concentration (mM Au(0); obtained from extinction at 400 nm²⁷) and the estimated volumetric mass density (effective) of nanoparticles (with 95% confidence bounds found by a heuristic search method⁵²). (b) Estimated percentage of electromagnetically interacting particles out of the overall population (*i.e.*, interacting + noninteracting) along with the respective 95% confidence bounds.⁵² (c) Mean centre-to-centre distance between electromagnetically interacting nanoparticles both normalized to the average particle radius and in absolute units (with 95% confidence bounds⁵²). (d) Experimental extinction spectra at selected temporal points. (e) Temporal evolution of peak width at half-maximum obtained from experimentally measured spectra.⁵⁴ (f) *In situ* measured solution pH and reduction potential (Eh vs. Ag/AgCl/c(KCl) = 3 mol/L). The grey-to-white shaded regions (all the plots except for (d)) characterize various mechanistic steps (denoted by Roman numerals in the first plot) as discussed in the main text.

Figure 7. Proposed mechanism for the seeded growth of gold nanoparticles with a schematic representation portraying the sequence of processes encountered during the seeded growth of GNPs in the experiment 15:85-70°C. The degree of overlap between primary particles inside secondary particles correlates with the effective density of the latter (*i.e.*, more overlap means a higher effective density).

Seeds and final grown GNPs are shown as individual particles to denote coalescence into single entities. Molecular growth happens throughout the process as represented by the continuous dashed arrow. To save space, the relative size of superclusters is not drawn to scale (they should be much larger than the individual secondary particles).

Figure 8. Coefficients (a) and scores (b) from principal component analysis on temporal UV-Vis spectra (15:85-70°C experiment). Legends are common in both plots. The grey-to-white shaded regions in part b characterize various mechanistic steps (denoted by Roman numerals) as discussed in the main text.

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Initial treatment of spectral
data (spectraTreatment.m)

Calibration of parameter η ($= \eta_0 + \eta_1 \bar{r}_{GNP}$) using average sizes estimated by TEM for seeds and final grown GNPs (optimSeedsGrown.m)

Regression using Gans theory
(optimNoninteract.m):
 $Ext = C_t l \sigma_{Gans} / \ln(10)$

Regression using GEM model
(optimGEM.m):
 $Ext = [C_t l / \ln(10)] \times [(1 - x_{SC}) \sigma_{Gans} + x_{SC} \sigma_{EMT/Mie}]$

Selecting superior model
using criterion in Supp. Eq. 5
(paperFigs.m, lines 15-81)

Optional: refining GEM regressions
for spectra with weaker interaction
effects (typically at the beginning
and close to the end; optimGEM.m)

Plotting optimization
outputs (paperFigs.m)

ACI Page Optimization

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Boundary of liquid-
like supercluster

Secondary particle
(agglomerate/aggregate)

t = 0 s:
seed
suspension

t = 20 s: primary
& secondary
nucleation

Reg. (I): onset of
electromagnetic
interaction

Reg. (II): primary
& secondary
nucleation

Reg. (III):
agglomeration

Reg. (IV): primary &
secondary nucleation
+peptization

Reg. (V): Ostwald/
interparticle
ripening

Molecular growth